The University of Chicago

THE EXISTENCE OF HOMOGENEOUS GROUPS OF LARGE IONS

A DISSERTATION

SUBMITTED TO THE FACULTY
OF THE OGDEN GRADUATE SCHOOL OF SCIENCE
IN CANDIDACY FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

BY

OSWALD HANCE BLACKWOOD

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Reprinted from
THE PHYSICAL REVIEW, N.S., Vol. XVI, No. 2, August, 1920

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THE EXISTENCE OF HOMOGENEOUS GROUPS OF LARGE IONS.

BY OSWALD BLACKWOOD.

SYNOPSIS.

Non-existence of groups.—Certain observers have found evidence indicating that the large ions produced by spraying water constitute several distinct groups each having a definite mobility. Using an apparatus similar to theirs, the author fails to confirm this result but finds that the ions distribute themselves continuously over a wide range with all intermediate mobilities present. In other words, he finds a *continuous* spectrum of mobilities and not a *band* spectrum. Conclusive proof of this has been obtained by a series of mobility determinations made with a Zeleney tube having a "resolving power" twenty times as large as that of the apparatus mentioned above.

Age and mean mobility.—The mean mobility of the ions decreases with time after formation at a rate indicating that the rate of condensation of water vapor on any ion is constant and independent of its size.

Growth of ions dependent upon the humidity of the air.—Having replaced the water sprayer by a red-hot platinum wire as a source of ionization, it was possible to control the water vapor density. Drying the air causes a decrease in the rate of growth of the ions.

Growth of ions probably due to condensation of water vapor.—The experimental facts are explained by assuming that large ions grow by condensation of water vapor on a nucleus. This assumption is consistent with the views as to the nature of the large ion held by Barus, Aitken, Thompson, and others.

NOLAN and McLelland[1] in 1916 and Nolan[2] in 1917 published papers presenting evidence which indicates that the spraying of distilled water or the bubbling of air through mercury produces large ions having a wide range of mobilities. The most mobile ion has a mobility much greater than that of the small ion produced in air by X-rays, while the most sluggish one approximates that of the stable Langevin ion found in the atmosphere. Moreover, the mobilities do not distribute themselves continuously over this range but constitute several distinct *groups*

[1] Proc. Roy. Irish Acad., Vol. 33, p. 9, p. 24, 1916.

[2] Proc. Roy. Soc., A, Vol. 94, 1917.

with intervening gaps. In other words, there seem to be band spectra of mobilities and not continuous spectra.

Recently the investigation has been extended, and similar indications have been found with regard to the ions produced by bubbling air through alcohol[1] or by passing it over phosphorus.[2]

TABLE I.

Water (Spray), *A*.	Mercury.				Alcohol, *F*.	Phosphorus, *G*.
	Ions Newly Produced.		Long Time Interval.			
	B, Undried Air.	*C*, Dried.	*D*, Undried Air.	*E*.		
6.5[1]						
3.27						
1.56						
1.09					1.10 ?	
.53					.50	
.24					.22	.22
.12					.12	
						.092
.046			.043	.043	.049	.053
		.024				.028
.013	.014		.02		.017	.018
		.0068		.0064	.0077	.0074
.0043	.0040		.0045		.0040	.0041
		.0021		.0022	.0023	.0024
.0010	.0013	.00	.0013		.0014	.0012
		.00056			.00063	.00064
.00038	.00034				.00034	.00031
					.00015	.00015
						.000085
						.000053

Table I. gives a list of the mobilities of the groups produced by each method. In column *A* it will be noticed that the first two groups have mobilities greater than those of the small ions produced in air by X-rays. Column *G* gives a list of mobilities of the groups produced by passing air over phosphorus. This list is highly significant because the range of mobilities is large, and because the fourteen mobility values constitute an approximate geometric progression.

In view of the fact that no plausible hypothesis has been suggested to account for the production of several classes of ions of which the mobilities form a geometric progression, the groups have seemed especially worthy of investigation. In order to test out the apparatus before attempting to discover whether the groups exist in the ionization pro-

[1] Proc. Roy. Irish Acad., A, Vol. 34, p. 57, 1918.

[2] Ibid., A, Vol. 35, p. 1, 1919.

duced by other methods; Nolan's work on the mobilities of the ions produced by spraying distilled water was repeated with slight modifications of apparatus to be described later. The author, to his surprise, failed to confirm the existence of the groups.

The apparatus first used was essentially that of McLelland and Nolan and is shown in Fig. 1. The parts requiring especial notice are:

1. The air pressure regulator, *A*.
2. The sprayer, *C*.
3. The capillary *C'*.
4. The ion testing tube *F*.

1. The air pressure regulator *A* is a vertical tube partly submerged in water. The bubbling of air escaping from the lower end of this tube keeps the pressure approximately equal to the water pressure at that end.

2. The sprayer *C* was made entirely of glass and was especially designed for this investigation. With an excess air pressure of one half atmosphere—the value used in all the measurements—a dense fog of spray is produced and the quantity of air required is only 30 c.c. per second.

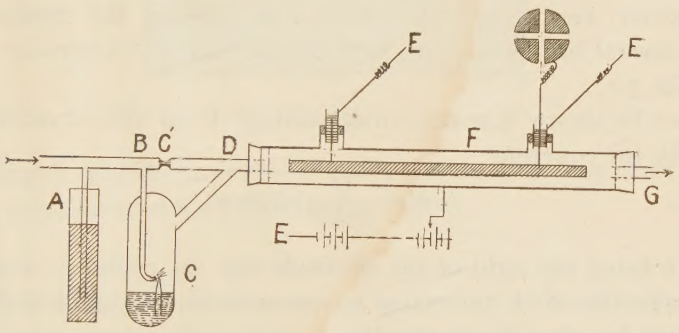

Fig. 1.

3. The capillary tube *C'* may be replaced by others of different bores, thus varying the velocity of the air current at will, while keeping the air pressure constant.

4. The ion testing tube *F* consists of a brass cylinder 160 cm. long and 5 cm. internal diameter, fitted with a co-axial cylindrical brass electrode 140 cm. long and 2 cm. in diameter. This electrode is supported by sulphur plugs mounted in grounded guard-rings. The electrode is connected to a pair of quadrants of a Dolezalek electrometer having a sensitiveness of 70 cm./volt with the scale at a distance of 200 cm. The outer cylinder may be connected to any portion of a battery of 100 fresh dry-cells.

On occasion, the rate of flow of air through the apparatus may be measured by attaching the tube of a gasometer at *G*.

METHOD OF EXPERIMENT.

Air from the laboratory system is filtered by passing it through a tube packed with glass wool. At B, Fig. 1, the stream is divided, part going through the sprayer C and part through the capillary C'. Reunited at D, the air enters the ion testing tube F.

The ion testing tube of the type described was designed by McLelland and has been used extensively in the determination of mobilities of large ions. These ions are carried forward in the tube by the air current and are simultaneously deflected toward the central electrode by the electric field. If the intensity of the electric field be gradually increased, the ion current to the electrode increases until the field becomes intense enough to drive all the ions to the electrode, beyond which point the current is saturated. It can be shown that—neglecting the effects of diffusion, recombination and distortion of the fields by electrode supports and by the presence of the ions—if ions of only one mobility are present the current-voltage curve is a straight line through the origin, breaking sharply at the critical voltage and becoming parallel to the voltage axis. If, however, ions of several mobilities are present, the resultant curve shows several breaks in slope, each corresponding to a certain mobility. (See Fig. 5.)

It can be shown that the critical voltage V for ions of mobility K is given by the equation[1]

$$k = \frac{Q}{2\pi LV} \log_e b/a$$

a and b being the radii of the electrode and the cylinder, respectively, Q the quantity of air traversing a cross-section of the tube each second, and L the length of the electrode.

SOURCES OF ERROR.

In the early observations much error was caused by the falling voltage of the accumulators. The charge induced on the central electrode by a decrease of only 1/5 volt, in a total of 160 on the outer cylinder, caused an electrometer deflection of several centimeters. This variation became negligible when the accumulators were replaced by dry cells.

A persistent error was due to the variations of the sprayer. Consecutive readings usually agreed within two per cent., but the positions of

[1] This formula becomes exact for a cylinder of finite length if the part $\frac{\log_e b/a}{2\pi L}$ be replaced by the *measured* capacity of the portion of the insulated system which is exposed to the air current. See W. F. G. Swann, "The Theory of Electrical Dispersion into the Free Atmosphere," Terrestrial Magnetism and Electricity, Vol. 19, pp. 81–88, 1914.

the breaks in slope of the current voltage curves shifted to such an extent in successive curves that it was usually impossible to determine mean curves showing breaks. (See Fig. 2.) In the effort to eliminate

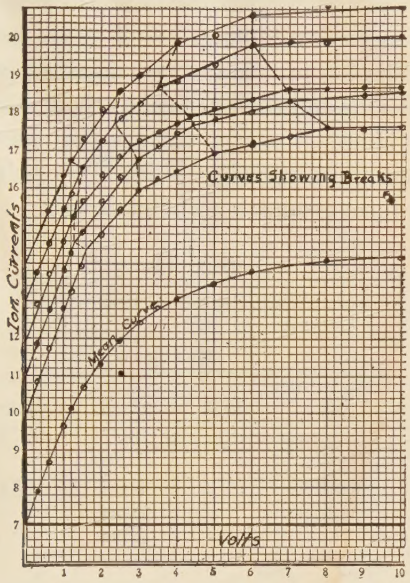

Fig. 2.

this shifting, three different types of medicinal sprayers were tried before the glass one already described was constructed.

Results.

In certain cases the current-voltage curves are quite smooth. (See Fig. 3.) In others breaks in slope are present which are quite as definite as those exhibited by Nolan. (See Fig. 5.) His value for the ratio of successive mobilities, however, is not found in a single instance. This

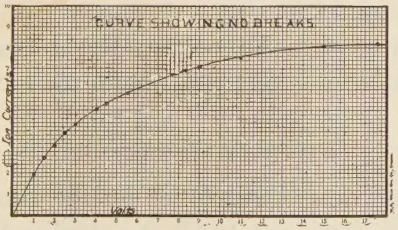

Fig. 3.

ratio, in the present investigation, is usually about 2.0 and is never as high as 3.4, the mean value determined by him.

Being convinced that the mobility values did not fit into the group system of Nolan, an attempt was made to ascertain whether my values determined from day to day fitted into any group system. Fifty-nine breaks were worked over in detail using various values of the air velocity and, in certain instances, introducing metal tubes between the sprayer and the testing cylinder in order to increase the time intervening between the production of the ions and their arrival at the testing tube. Table II. shows the mobility values. For convenience they have been arranged in classes, but if they are represented graphically by points along a straight line no tendency to form groups is to be observed.

TABLE II.

Mobility Values Determined by the Author.

Time After Production.	Mobilites of Ions.						
60 sec.		.0016	.0027	.0036 .0037	.0080 .0070	.016 .017	.028 .037
100 "	.0006	.0013 .0017		.0042 .0035 .0043	.0082	.012 .013 .014	
600 "	.0003 .0006	.0010 .0011	.0020 .0022 .0027	.0043 .0045	.0080		
1200 "	.00055 .00046 .00077 .00080	.0011 .0012 .0010 .0010	.0016 .0014 .0017 .0021 .0020 .0026	.0045 .0039 .0030 .0037 .0036 .0042 .0053	.0070 .0060 .0065 .0060	.015	

If then we disregard breaks, the smooth curve may indicate either a continuous distribution of mobilities or it may indicate that the sharpness of the break in the theoretical curve for a single class of ions has been obscured owing to the failure to obtain the ideal conditions of the theoretical method.

CRITICISM OF METHOD.

The McLelland ion tube is well suited for the measurement of mobilities which are widely separated, but if the number of breaks is large the distance between breaks is small and, owing to experimental errors, a smooth curve results. In the investigations carried on by McLelland and Nolan, in most instances not more than six breaks were located for

any individual current-voltage curve. It will be of interest to see how little such a curve differs from a smooth one corresponding to a continuous distribution of mobilities. Fig. 4 is a theoretical curve showing breaks corresponding to six different classes of ions all present in equal concentrations. The ratio of each mobility to the one preceding it is 1.9 which is the approximate value found by McLelland and Nolan for the ions produced by passing air over phosphorus. It will be noticed

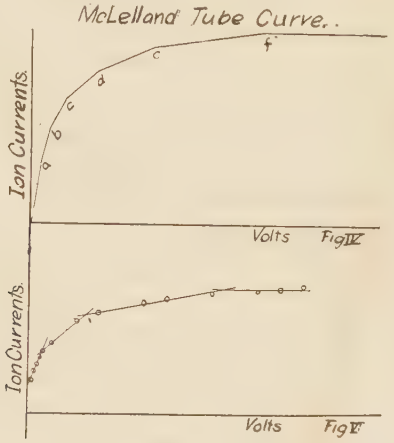

Fig. 4.

Theoretical Curve Indicating Existence oi Groups.

Fig. 5.

Experimental Curve Determined by Nolan.

that the breaks, especially (*a*), (*b*), and (*c*) are so slight that they would easily be masked by experimental errors.

Nolan himself admits the possibility of a smooth curve being drawn through his points. Regarding the only curve showing several breaks which he exhibits (see Fig. 5), he writes:

"It might be said that a smooth curve might be drawn with almost equal exactness, showing that, instead of an abrupt step in mobilities, there was a gradual shading off from one to another, with ions of all intermediate mobilities present. With the object of eliminating this sort of uncertainty, and of obtaining as accurate values as possible for the mobilities of the different ions, the current-voltage curve was worked over in detail many times, each section being investigated under conditions specially chosen to bring out its features."[1]

It is on the evidence of such breaks as these that Nolan in his earlier paper, based the claims for the existence of positive and negative ions

[1] Proc. Roy. Irish Acad., A, Vol. 33, P. 12, 1916.

whose mobilities are higher than any previously discovered for normal ions generated by X-rays, ultra-violet light, etc. To the writer's knowledge such abnormally high mobilities for positive ions have never been found by other observers though methods of much higher sensitiveness have been used, and though the experiments have been carried out not only in the prsence of water vapor but also in carefully dried air in which the mobilities are distinctly higher. It is indeed true that abnormal mobilities have been found in the case of negative ions at low pressures for common gases, and even at atmospheric pressures for monatomic gases. These high mobilities, however, are believed to be due to the presence of free electrons.

In a more recent investigation[1] having modified his apparatus by replacing the cylindrical ion tube by a plate condenser, and by introducing the nozzle of the sprayer directly into the field between the plates, Nolan obtains discontinuities in his curves of an entirely different order of magnitude from those which occur in the earlier experiments. These discontinuities are certainly of a real nature and it is not in questioning their existence that one can attempt to correlate the present results with those of Nolan. It must, however, be pointed out that the breaks in his current-voltage curves may be produced as well through discontinuous changes in the electric fields driving the ions to the electrode as by a discontinuous distribution of mobilities of the ions themselves. The possibility of such an explanation of the curves of Nolan seems worthy of discussion. He himself admits regarding the observational values of his field strengths, that the applied voltage differs from that corresponding to the effective values of the fields by from zero to 4.5 volts. It is noticeable, also, that the discontinuities in the ion currents are comparable in magnitude to possible sudden changes in potential of the same order of magnitude as the values of the uncertainties in the potential difference which Nolan admits. Exactly how these discontinuities might occur, one cannot decide. It is possible that in increasing the negative value of the field strength, different sizes and different positively charged droplets produced by spraying, are successively removed from the space between the electrodes, thus discontinuously changing the values of the field. Nolan himself states that the uncertainty in his fields can be explained on the assumption of the disappearance of small positively charged droplets from between the plates. It is also to be noted that he obtains values of the positive and negative mobilities which are many times as great as the values obtained in dry air by the classical methods. It seems possible that the explanation of these mobilities

[1] Proc. Roy. Soc., A, Vol. 94, 1917.

lies in the fact that the absolute values of his fields are not definitely known. For example, for a negative carrier whose mobility he gives as 188 cm./volt × volt/cm. he finds that the break in his curve occurs at +3.5 volts. When the potential of the lower plate is further increased to +3.75 volts, no negative ions from the sprayer reach the upper electrode and the electrometer current becomes zero. Nolan assumes, therefore, that at +3.75 volts the field driving the negative ions toward the upper electrode is zero. What the experiment shows, however, is not that the field is zero, but that it is not strong enough to drive the ions to the upper electrode before they are carried past the electrode by the air current. The ions are probably driven *toward* the upper plate even though they do not actually reach it. For his experimental arrangement he finds $Vk = QA/LB = 47$ (in which A, L, B, are the dimensions of the plate condenser, Q is the quantity of air traversing it each second, k the ionic mobility, and V the potential difference between the plates). Having assumed that the critical voltage $(+3.75 - 3.50) = +0.25$ is necessary to drive the ions across the distance between the plates in the time during which they travel the length of the condenser, he interprets the mobility k as being equal to $k = 47/(3.75 - 3.50) = 188$. If one assumes under these conditions that he was actually measuring the mobility of the normal negative ion, which is 1.8, the same initial break in the curve could have been caused if the actual value of the field were $47/1.8 = 26$. This field strength could possibly have been caused by the electrification of the air produced by the sprayer which, as has been stated, is introduced directly between the plates of the condenser. As in his paper no mention is made of an attempt to verify the values of the fields by exploring electrodes or otherwise, there seems to be no apriori reason why one interpretation of this result is not just as adequate as the other. Too much confidence, then, cannot be placed on the interesting results of Nolan until there is more certainty as to the values of his fields.

The Zeleney Method.

It was obvious that, using the method of McLelland and Nolan no positive decision as to the real existence of the groups of ions could be obtained. Recourse was accordingly had to a modification of the Zeleney method which seems much better adapted for giving a decisive verdict.

The electrode of the ion tube already described was cut into two sections L' and L'', 105 and 35 cm. long respectively, which were separated by a small air gap. The electrode L' was grounded and L'' was connected to the electrometer. (See Fig. 6.)

THEORY.

The ions, produced in the same manner as that described in the previous section, are carried by the stream in a direction parallel to the axis of the tube. Disregarding diffusion, if there is no potential difference between the outer and inner cylinders, none of the ions will reach the inner electrodes. If, now, the outer cylinder be raised to a potential

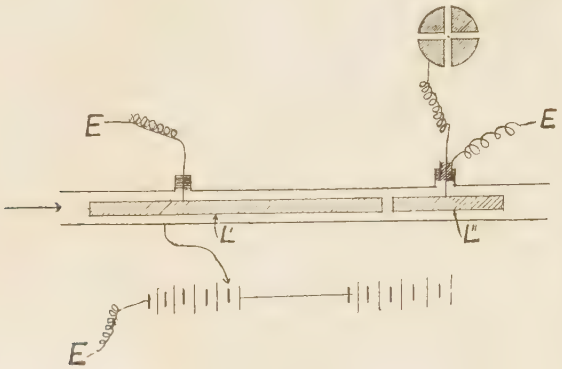

Fig. 6.

above the inner ones, all the positive ions entering the tube within a distance r of the axis are driven to the electrodes, while all others escape. As the potential difference increases, the value of r also increases and, consequently, with it the ion current to the electrodes. At a critical voltage V', r becomes equal to the radius of the cylinder and all the ions are driven to the electrodes so that the current reaches its maximum. As the potential difference is still further increased, more and more ions are driven to the first, grounded, electrode, and consequently the electrometer current from L'' diminishes until, at a second critical voltage V'', it becomes zero.

Neglecting the influence of recombination and diffusion of the ions, and assuming that the electric field is radial at all points in the tube, it has been shown that the Zeleney tube gives a current-voltage curve of the form shown in Fig. 7 (C).[1] The nature of this curve may be deduced from the curves A and B (Fig. 7) which are determined when the electrometer is connected (as in the McLelland arrangement already described) (a) to the first electrode L' and (b) to both electrodes. The curve (C) of which the ordinates are evaluated by subtracting the corresponding ordinates of A from those of B, therefore represents the ion current to L'' when L' is grounded.

[1] Bloch, Ann. de Chemie et de Physique (8), Vol. IV, p. 25, 1905.

From the curves A and B it is evident that V' is the voltage causing saturation when the electrode has the length $(L' + L'')$ while V'' causes saturation using an electrode of length L'.

For ions of mobility k, we have in the two cases:

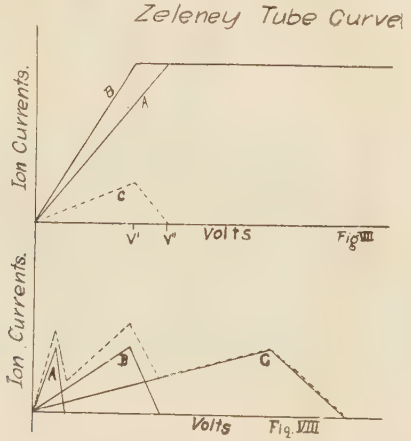

Fig. 7. Fig. 8.

$$k = \frac{Q \log_e b/a}{2\pi(L' + L'')V'} = \frac{Q \log_e b/a}{2\pi L' V''} ; \qquad (1)$$

$$\therefore \quad \frac{V'}{V''} = \frac{L'}{(L' + L'')} . \qquad (2)$$

The saturation voltage V' being given for ions of mobility k, it may be computed for ions of mobility K' from

$$k/K' = \frac{V_1'}{V'} . \qquad (3)$$

If the maximum ion current be known, the current-voltage curve for the Zeleney apparatus may be constructed for ions of a given mobility with the aid of equations (1), (2), and (3).

Figure 8 (A), (B), (C) shows the forms and relative positions of the current voltage curves of the Zeleney apparatus for ions of mobilities .0043, .0010 and .0004. These are three mobility values for successive groups as found by Nolan for ions from spray. The dotted line shows the summation curve determined if the ions of the three groups are present in equal concentration.

If the number of groups should increase, and the interval between successive groups consequently become smaller, the broken line would be less deeply notched and, if the ions did not constitute distinct groups but distributed themselves continuously over the range from .0043 to

.0004, the curve would be smooth as indicated by the dotted line in Fig. 9 *A*. To decide whether the groups exist or not, it is therefore sufficient to decide whether the experimental current-voltage curve has one or more than one maxima.

Similarly, Fig. 9 *B* shows the theoretical curve given by the McLelland tube if the same three groups of ions are present in equal concentration. The dotted line shows a smooth curve such as might be given by a

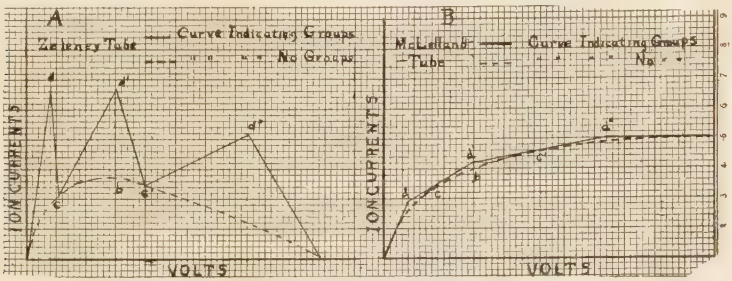

Fig. 9.

continuous distribution of mobilities. Comparing the curves *A* and *B* it is evident at a glance that the Zeleney apparatus affords a more decisive test as to the existence of the groups.

We shall arbitrarily define the "resolving power" of each instrument for any type of ions as the ratio bd'/cc' (Fig. 9 (*A*) and (*B*)). In the case of the three breaks in *each* curve, the "resolving powers" are approximately.

Group.		*d*.	*d'*.	*d''*.	Mean.
"Resolving Powers"	Zeleney Tube.....	2.	1.	½	1.2
	McLelland Tube.....	0.1	0.07	0.025	0.065

The resolving power of the Zeleney tube for the curves shown is accordingly about 18 *times as great as that of the McLelland arrangement.*

Measurements with Zeleney Tube.

Owing to the fact that the available time was limited, it was possible to determine only seven curves for spray ions using the Zeleney apparatus. In certain instances metal tubes were introduced between the sprayer and the ion tube in order to "age" the ions or increase the time interval between their production and arrival at the testing tube. Two specimen curves for different ages are shown in Fig. 10. Several interesting conclusions may be drawn from their forms and relative positions.

Non-existence of Groups.

The fact that this apparatus, having a "resolving power" many times greater than that of the McLelland arrangement, gives curves showing no discontinuities, seems conclusive evidence that a series of well-defined groups does not exist. Each curve shows one maximum and inversion point which indicates a preponderance of ions whose

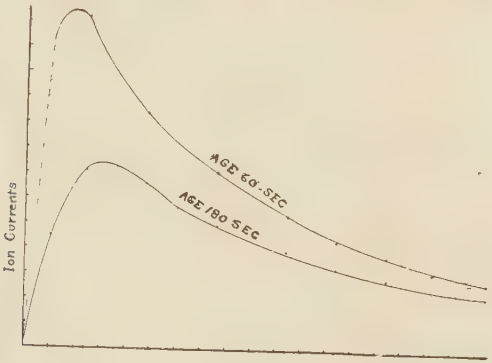

Fig. 10.

mobilities lie on a narrow range. The curves also show, by the fact that they approach the voltage axis asymptotically, that other ions of very low mobility are also present.

Effect of Ageing.

When tubes are interposed between the sprayer and testing tube to "age" the ions, the center of gravity of the curve shifts to the right, indicating that the mean mobility has decreased. This agrees with the observations of Nolan. He explains this decrease as due to the disappearance of the smaller ions owing to their diffusion to the walls of the containing vessel; to their recombination to form larger neuclei; or to their growth by condensation of water vapor.

A more striking series of curves was obtained when the sprayer was replaced by a red-hot platinum filament as a source of ionization. This wire was found to afford a copious supply of positive ions, but a negligibly small number of negatives.

In this case, as before, tubes were interposed between the sprayer and the ion testing cylinder in order to age the ions. Several curves for different ages are shown in Fig. 11. In view of the fact that a preponderance of the ions for any age have mobilities lying on a narrow range on either side of the mobility value for the ion which is present in greatest numbers, an effort was made to interrelate the ages with

the respective mobility values for the maximum-concentration ion. The critical voltage corresponding to the maximum ion current was therefore determined for each curve, and the mobility values were computed with the aid of equation (1). The results are shown in Table III.

If one plots the logarithms of the values of these mobilities as ordinates

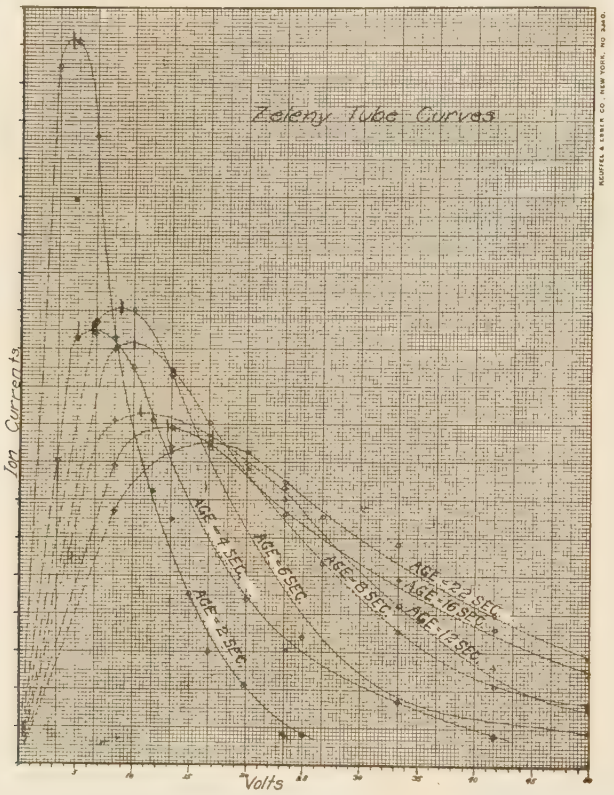

Fig. 11.

TABLE III.

Mobility Values for Ions Present in Greatest Concentration.

	Age.										
	2.	4.	6.	8.	12.	16.	22.	32.	45.	58.	70.
Mobility..	0.06	0.042	0.029	0.026	0.023	0.020	0.016	0.012	0.009	0.0075	0.0065
Log age ..	0.30	0.60	0.78	0.90	1.08	1.24	1.351	1.51	1.65	1.76	1.85
Log ($k \times$ 1,000)..	1.78	1.62	1.46	1.41	1.36	1.30	1.20	1.08	0.96	0.87	0.81

against the logarithms of the corresponding ages as abscissas, the points are found to lie sensibly along a straight line of which the slope is 6/10 (see Fig. 12). This differs from 2/3 by 10 per cent. If we assume 2/3 to be the correct value, we may interrelate the age of the ions with the mobility of the maximum-concentration ion as follows:

$$\begin{aligned} 3/2 \log k + \log t &= \log C, \\ k^{3/2} t &= C, \end{aligned} \tag{4}$$

in which k represents the mobility of the maximum-concentration ion, t the age of the mixture of ions (defined on page 12), and C is an empirical constant. If in accordance with the "hard elastic sphere" theory of J. J. Thompson[7] we assume that the mobility of a large ion varies inversely with its radius squared, equation (4) may be written:

$$\frac{C'}{4/3\pi r^3} \times t = C$$

or

$$t = C/C'v;$$

$$\therefore \quad dv/dt = C'/C,$$

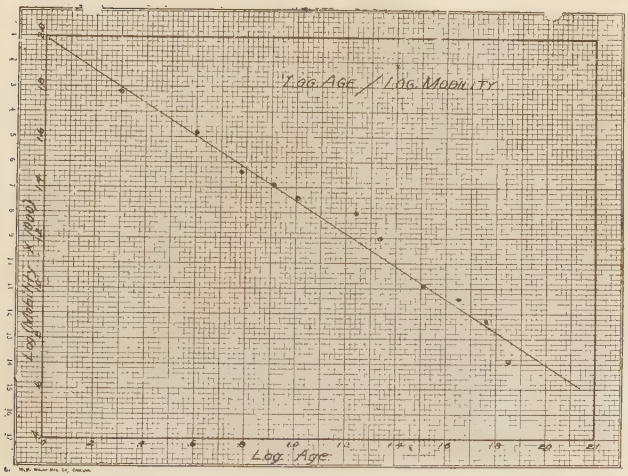

Fig. 12.

C' being a constant of proportionality, and v the ionic volume. This indicates that the ions are growing at a constant rate, independent of the radius.

[7] Thompson, Conduction of Electricity through Gases.

HUMIDITY AND RATE OF GROWTH OF THE IONS.

Using the hot-wire method of ion production, it was possible to control the water vapor density in the air which was driven through the ion tube. The air was dried by passing it over $CaCl_2$ and P_2O_5. The air was then charged with water vapor by bubbling it through a column of water, the temperature of which was raised in successive "runs," so as to increase the vapor density. It was found that for a given age increasing the vapor density decreased the mean mobility of the ions, which indicates that the presence of water vapor is favorable to the growth of the ions.

The conception which one gains from the above experiments as to the nature of the formation of the large ions is consistent with the views published in the papers of Barus,[1] Aitken,[2] Pollock,[3] Lenard,[4] and others. It is not at all inconsistent with the experiments of C. T. R. Wilson as explained by Thompson.[7] According to our results, the original nucleus of the large ion may be an agglomeration of a few molecules of water or a few particles of dust which have gathered a charge either in the process of formation (spraying of water), or by picking up a charge while passing through the ionized gas surrounding the hot platinum filament. These nuclei, due in part to their charge, may continue to grow by condensation of water vapor or by agglomerating into larger units, at a rate depending on the concentration of water vapor and on the time interval in which the ions have had a chance to reach equilibrium. The detection of the particle or nucleus as an ion, and possibly to some extent, its dimensions, are dependent on its acquiring a charge at some stage of the process. The explanation of these results in no way demands the growth of the large ion through the clustering of water molecules around a single charge.

SUMMARY.

I. Using the McLelland method for the determination of mobilities of large ions, it is shown by a series of experimental curves that we are not justified in concluding that a series of groups of ions of definite mobility exist.

II. It is also shown that the breaks in the curves obtained by the author which indicate the existence of groups of definite mobility, are too uncertain to permit of their interpretation in this way in view of the possible magnitude of experimental errors.

III. It is also pointed out that the experimental curves obtained by

[1] Amer. Jour. Science, 33, p. 107, 1912.

[2] Aitken, Roy. Soc. Edinburgh Proc., 37, p. 215, 1916–17.

[3] Pollock, Phil. Mag., Vol. 29, p. 514, 1915.

[4] Lenard, Ann. Physik, Vol. 47, 44. July, 1915.

Nolan in a more recent paper in which the breaks are unquestionably present, may be interpreted in other ways not involving the assumption of the existence of groups of ions of abnormally high mobilities.

IV. The problem was also attacked using the Zeleney method of mobility measurement which gives a much higher "resolving power," than the McLelland method, with the result that no evidence was found for the existence of groups of ions of several different mobilities.

V. Further results are given showing a relation between the mean mobility of the ions present and the time which has elapsed between the formation of the ions and the measurement of their mobility, in the case of ions formed by spraying water and from hot wires. These results indicate that the mobility varies as the 2/3 power of the reciprocal of the age, from which it is deduced that the rate of growth of the ions is constant.

In conclusion I wish to express my gratitude to Dr. Millikan under whose direction this investigation has been carried out, to Dr. A. J. Dempster for occasional assistance, and to Dr. Leonard Loeb for aid in the interpretation of results and the revision of my manuscript.

Ryerson Physical Laboratory,
January 5, 1920.